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IMPEDANCE STUDIES OF THE CELL AG/AG BETA' ALUMINA/AG

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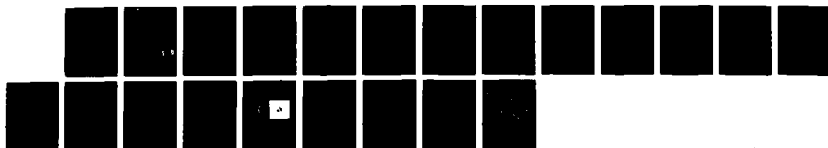
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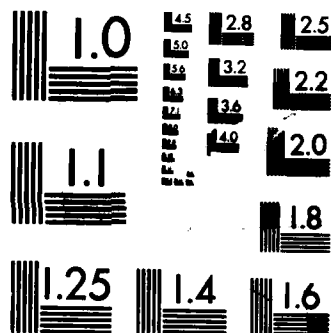
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Impedance Studies of the Cell Ag/Ag Beta" Alumina/Ag

by

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Impedance Studies of the Cell Ag/Ag Beta"Alumina/Ag *

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ABSTRACT.

Measurements of the cell impedance were carried out at constant temperature between 25 and 450°C at frequencies between 10^{-2} and 10^4 Hz. The surfaces of the solid electrolyte which was obtained by exchanging the sodium ions of the starting material, Na beta"alumina from Ceramatec Inc., by silver ions in molten AgNO_3 were either polished or saw-cut. Silver electrodes were attached by silver paint after applying the initial silver layer by sputtering. The silver electrodes display the behavior of a blocking electrode in a wide frequency range at temperatures below about 200°C. This behavior is clearer pronounced on the polished surfaces. The saw-cut surfaces show an intermediate behavior between blocking and non-blocking electrodes. A transition from blocking to non-blocking electrodes occurs between 150 and about 200°C for both types of surfaces. The impedance data are analyzed in the lower temperature range by an analogue network.

* Dedicated to Prof.H.Gerischer

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INTRODUCTION.

The impedance of the cell Ag/Ag beta"alumina/Ag was investigated for the following reasons:

1) It is a relatively simple system, involving a solid electrolyte of the beta alumina group¹ with the one-valent silver ion as the conducting species and silver metal as electrodes. The cell is symmetric with respect to the electrodes. Information about the behavior of the interface Ag/Ag beta"alumina as a function of temperature should be deducible.

2) When using silver contacts in four-probe measurements² of the ionic conductivity of Ag beta"alumina at 10^3 Hz, a change in the properties of the contacts was observed to occur in the temperature range between about 100 and 200°C. This indicated that a change in the properties of the interface, possibly the transition from silver as a blocking electrode to silver as a non-blocking electrode, occurs.

3) Since Ag beta"alumina does not pick up water to a noticeable extent^{3,4}, the interpretation of the impedance measurements is not complicated by additional electrochemical processes, due to water or hydronium ions⁵.

Impedance measurements⁶ proved very useful in the study of electrode kinetics in aqueous solutions. An excellent review of the application of this technique to solid electrolytes is given in ref.7. Here the results of the impedance measurements with the said cell in the frequency range 10^{-2} to 10^4 Hz and temperature range 25 to 450°C will be presented. Two types of surfaces of the solid electrolyte were used: saw-cut and polished. The solid electrolyte was polycrystalline.

EXPERIMENTAL SECTION.

Pieces of rectangular cross section (1cm X 1cm) and a thickness of about 0.5 cm were cut from bars of polycrystalline Na beta" alumina, supplied by Ceramatec Inc. The nominal composition of this starting material was: 90.4% Al_2O_3 , 8.85% Na_2O , 0.75% Li_2O . The sodium ions were replaced by silver ions by immersing the samples for 24 hours in molten AgNO_3 at 250°C . The completeness of the ion exchange was monitored by the weight change. As demonstrated recently⁸, the weight change allows to compute the extent of exchange in a good approximation for polycrystalline Ag beta"alumina.

Some of the exchanged samples were polished on both large sides to $1\text{ }\mu\text{m}$. Silver films were sputtered onto these sides of the polished and unpolished specimens. The thickness of these films was 10 to 50 nm. Silver paint was applied afterwards. The silver paint dried for 24 hours in air and for 24 hours at about 200°C . Silver nets were attached by silver paint, using the same drying process as before. The nets were cut in such a way that they consisted of square pieces (1cm X 1cm) for contacts and rectangular pieces (0.2cm X 1cm) for leads. Flat pieces of alpha alumina were pressed against the silver nets. Tungsten wire was wrapped around the cell to keep it together. The rectangular pieces of silver net were hooked up to the relatively thick Ag wires of the measuring cell by brass connections with screws. A schematic diagram of the cell and a photo of the actual cell are shown in Fig.1.

The measurements were carried out inside a Pyrex glass vessel, flushed by nitrogen. The glass vessel had a lid with a removable large joint through which the silver wires were

introduced by smaller joints. The removable large joint allowed to mount the Ag/Ag beta"alumina/Ag cell on the outside. The glass vessel was inside a small furnace heated by DC current. The furnace and the lid of the glass vessel were well insulated. The temperature was maintained at a desired value by a temperature controller. Sufficient time was allowed for temperature equilibration between individual runs. The use of DC current significantly reduced the noise which is introduced from the net in the case of AC heating.

The measurements of the cell impedance were carried out at constant temperature, starting out with room temperature and subsequently going to increasingly higher temperatures. The automated impedance meter IM 5E, produced and sold by Zahner-elektrik in West Germany, was employed. The frequency range covered 10^{-2} to 10^4 Hz in this study.

EXPERIMENTAL RESULTS.

Impedance spectra for the cell Ag/Ag beta"alumina/Ag with polished surfaces of the solid electrolyte are shown for 50, 250 and 400°C in Fig.2. The data are presented in a Bode plot. The automated impedance meter yields the data in this form. An attempt to obtain the data in a Cole-Cole plot was not undertaken. At present it requires the manual transfer of the data to another computer by which the Cole-Cole plot is produced. Work is in progress to develop a technique of automated transfer of the data.

The respective data for the said cell with saw-cut surfaces of the solid electrolyte are contained in Fig.3. As in Fig.2 the three temperatures were chosen as representative for the

temperature dependence of the behavior of the interface.

DISCUSSION.

General Considerations.

An attempt will be made to interpret the frequency dependence of the impedance of the cell Ag/Ag beta"alumina/Ag at constant temperature by the network in Fig.4. The meaning of the ohmic and capacitive elements in this network will be given later. The following basic assumptions are involved:

- a) The surfaces forming the interfaces Ag/Ag beta"alumina are smooth and homogeneous.
- b) The frequency range is chosen such that the bulk impedance⁷ can be represented by the ohmic resistance R5, e.g. the contribution of the capacitive component of the bulk impedance, due to grain boundaries, is negligible.
- c) The absolute value of the cell impedance is low enough that the contribution of the geometric cell capacitance⁷ which is parallel to R5 is negligible.

The assumptions b) and c) can be fulfilled by the choice of appropriate frequency ranges. Since Ag beta"alumina is a relatively good ionic conductor the condition b) holds for frequencies below 10^4 Hz. To check the fulfilment of condition c) the frequency dependence of different resistors with low inductance was measured as a function of frequency by the impedance meter. The phase shift due to capacitive effects was small at frequencies between 10^3 and 10^4 Hz if the resistance remained below $10^4 \Omega$. This implies that the geometric capacitance is negligible in the frequency range of this study. It should be pointed out that the contribution of the geometric capacitance is

inversely proportional to the frequency. Therefore larger absolute values of the cell impedance can be measured at lower frequencies. The assumption a) is very questionable because the polycrystalline Ag beta" alumina itself is not a homogeneous material. It contains a small percentage of the beta alumina phase and of aluminate. In addition there are closed-ended pores originating on the surface⁸. The applicability of assumption a) to the present system will be discussed in connection with the experimental results.

The network in Fig.4 is useful for two special cases:

d) Blocking electrode.

e) Non-blocking electrode.

The meaning of the components in the network differs for cases d) and e). In case d) an electrochemical reaction does not occur to a noticeable extent. The adsorption capacitances C2 and C7 are small. The sums (R1 + R3) and (R6 + R8) correspond to the ohmic component of the double layer impedances. C4 and C9 are the double layer capacitances. Models which take account of the roughness of a surface have been suggested^{7,9}. In addition, a distribution of the sites was considered⁹.

In case e) the influence of the ohmic component of the double layer impedance is neglected. C4 and C9 have the same meaning. R3 and R8 are charge transfer resistances of the reaction :



R1 and R6 represent the resistances due to a possible adsorption reaction involving silver ad-atoms in the present study.

The intermediate case between d) and e) is difficult to describe by the network in Fig.4. It is not certain how to take account of the ohmic component of the double layer impedance. It

will be shown subsequently that the case d) corresponds in a first approximation to measurements in a certain frequency range at temperatures below about 200°C. At temperature above 200°C the case e) is applicable. Therefore the subsequent discussion is divided into a section dealing with the measurements below 200°C and another section for higher temperatures.

Behavior of the Electrochemical Cell below 200°C.

The data at 50°C are presented in Fig.2 as an example for the behavior of the cell Ag/Ag beta"alumina/Ag with polished surfaces at temperatures below about 200°C. The cell impedance Z_{cell} can be approximated in a wide frequency range (10^0 to 10^3 Hz) by the equation:

$$(2) \quad Z_{\text{cell}} = B(j\omega)^{-n}$$

Here B is a constant and n has values between 0 and 1. From a practical point of view the n values varied⁹ between about 0.9 at room temperature and 0.6 at 400°C for the system Pt/Ag beta"alumina/Pt. Usually a double-logarithmic plot of ohmic and capacitive component of the impedance versus the frequency is employed in the verification of Eq.2. The double-logarithmic plot is not as sensitive as the plots of phase angle versus logarithm of frequency of this study. A look at the data in Fig.2 at 50°C demonstrates the latter point. The absolute value of Z_{cell} can be approximated by a linear function in a wider frequency range than the range in which the phase angle is nearly constant. The determination of n from the data between 10^0 and 10^3 Hz in Fig.2 leads to 0.90. This value is close to the one quoted in ref.9 for the system Pt/Ag beta"alumina/Pt with polished polycrystalline surfaces. Similarly, the present value of the constant D,

defined in table 1 of ref.9, differs only by a factor 2 from the one quoted there. The great sensitivity of the Bode plots also revealed that the wide frequency range of nearly constant phase angle, observed at 25 and 50°C, splits into two regions at 100 and 150°C. The phase angles are nearly constant in each of the two regions, but differ somewhat. It was already concluded⁹ from the temperature dependence of n that the surface is composed of many areas with different n values. This conclusion is confirmed here.

As it is discussed extensively in ref.9 in which references to earlier work of the same nature can be found, the frequency dependence in Eq.2 is characteristic for that of the interface between a blocking electrode and a solid electrolyte. Possible models which consider the effect of the surface roughness and lead to Eq.2 are described there⁹.

Systematic deviations in the ohmic component of the cell impedance from the behavior according to Eq.2 are observable at frequencies between 10^3 and 10^4 Hz in Fig.2 at 50°C. As for the cell Pt/Ag β -alumina/Pt in ref.9 the deviations at high frequencies are ascribable to the fact that the ohmic component approaches the DC resistance of the solid electrolyte, e.g. R_5 in Fig.4.

The inaccuracy of the determination of the ohmic component at low frequencies and phase angles close to 90° was considered responsible⁹ for the deviations in the low frequency range (10^{-1} to 10^1 Hz) in the system Pt/Ag β -alumina/Pt. The present measurements on the system Ag/Ag β -alumina/Ag suggest that the deviations in the low frequency range are of a systematic nature and cannot only be assigned to inaccuracies. The phase angle decreases rapidly from a value close to 90° to a

smaller value. This deviation of the experimental data from Eq.2 is discussed in the next paragraph. It should be pointed out that the employment of Ag electrodes is also mentioned in ref.9. However, experimental data or information on the type of cells with Ag electrodes are not given.

The network in Fig.4 corresponds to $n = 1$ of Eq.2. It might hold approximately for the data in Fig.2 at 50°C since the measurements between 10^1 and 10^3 Hz demonstrate a nearly constant phase angle close to 90° and the deviations at frequencies above 10^3 Hz can be attributed to R_5 . Assuming that the impedance of the double layer can also be described in a first approximation by a capacitance at low frequencies, an attempt was made to determine the values of the components of the network in Fig.4. This was done by an optimization program delivered by Zahner-elektrik. Every second experimental point was used in the optimization. Principally, the question arises to what extent the determination of a large number of parameters (here : 9) from the experimental data can be meaningful for the validation of a model. Fortunately, the number of parameters reduces itself here. Owing to the similar preparation of the interfaces it can be assumed that the cell is symmetric, e.g. $R_1 = R_6$, $R_3 = R_8$, $C_2 = C_9$. A correct optimization should give numerical values for the components of the network reflecting the said symmetry. Finally it can be estimated if R_5 has a reasonable value by comparing it with the value for the bulk resistance, computed from the geometric dimensions of the sample and the four-probe conductivity. The word "estimated" was used here since the appearance of a phase angle during the four-probe measurements² of the bulk conductivity does not allow the exact determination

at low temperatures.

The result of the computation is shown by the solid curve in Fig.5. An approximate fit is achievable. However, the theoretical curve shows a small peak which does not exist at low frequencies in the experimental data. Symmetrical elements have similar values. The value of R_5 (bulk resistance) is reasonable. The values for the double layer capacitance (C_4 and C_9) are small with $3 \cdot 10^{-8} \text{ F/cm}^2$. The values of C_2 and C_7 with $6 \cdot 10^{-8} \text{ F/cm}^2$ are comparable to those for the double layer capacitance and indicate in the frame of the model that there are few Ag ad-atoms. Results similar to those in Fig.5 were obtained when applying the optimization program to other measurements below about 200°C . The following interpretation is advanced: The interface Ag/Ag beta"alumina with polished surfaces displays the behavior of a blocking electrode at frequencies between 10^0 and 10^4 Hz in the said temperature range. At frequencies between 10^{-2} and 10^0 Hz the effect of reaction 1 has to be considered. Probably the behavior corresponds to the intermediate situation between the limiting cases d) and e).

The results in Fig.3 at 50°C were obtained with saw-cut surfaces. The data might be described in a rough approximation between 10^{-2} and 10^1 Hz by Eq.2 with a value of n close to 0.3. However, judging from the relatively small change of the values of n in Table 1 of ref.9 for the transition from a polished to a saw-cut polycrystalline surface, the change from $n = 0.9$ to $n = 0.3$ appears too large. Computations with the optimization program for the network in Fig.2 were also carried out. They yielded the result that the values for symmetrical elements were not numerically close to each other for all the measurements below 200°C . The cell Ag/Ag beta" alumina/Ag with saw-cut surfaces

displays a more complicated behavior than that with polished surfaces. It is suggested that the "asymmetrical" behavior, indicated by the optimization program, reflects the presence of different sites on each of the two electrolyte surfaces and not a difference in the two interfaces. The superposition of many networks of the type in Fig.4 will lead to a flat curve for the phase angle. The absence of surface homogeneity for the saw-cut surfaces is responsible for the observed behavior. Since the surfaces are larger in the case of saw-cutting than of polishing, the experimental data demonstrate a stronger participation of reaction 1 in the former case. On the basis of the preceding discussion the results in Fig.3 at 50°C may be interpreted in a qualitative fashion. The intermediate case between blocking and non-blocking electrode is already observable at higher frequencies (10^1 Hz) on the saw-cut surfaces. The increase of the phase angle between 10^1 and 10^3 Hz indicates the transition to a more capacitive behavior as it is seen at lower frequencies on the polished surfaces (compare Fig.2, 50°C). The influence of the bulk resistance (R_5) is recognizable between 10^3 and 10^4 Hz.

Behavior of the Electrochemical Cell above 200°C.

A rapid transition from the behavior of the cell impedance in Fig.2 at 50°C to that in Fig.2 at 250°C occurs between 150 and 200°C for the cell with polished surfaces. It is this type of transition which becomes noticeable in the same temperature range during the four-probe measurements of the ionic conductivity of Ag beta-alumina with silver contacts for the voltage probes² at 10^3 Hz. While the phase angle amounted to 45° at 10^{-1} Hz at a

temperature of 50°C, it reaches 45° at about 200 Hz at 250°C. The cell impedance displays the more capacitive behavior at considerably larger frequencies. The decrease of the phase angle due to the influence of the bulk resistance occurs at higher frequencies than 10^4 Hz and is therefore not observable in Fig.2 at 250°C. The absolute value of the cell impedance decreases in the frequency range of more capacitive behavior. However, the ohmic component of the cell impedance does not yet reach the value of the bulk resistance, computed from the geometric dimensions and the four-probe conductivity. The transition to more capacitive behavior for the cell impedance moves to higher frequencies with increasing temperature and is not visible in Fig.2 at 400°C any more. The experimental results suggest that the change of the properties of the cell impedance between 150 and 200°C reflects the transition from the predominance of the behavior of a blocking electrode in a wide frequency range to the predominance of that of a non-blocking electrode.

The absence of the frequency range in which R5, C4 and C9 of the network in Fig.4 should make a large contribution reduces the applicability of this network for temperatures above 200°C. Nevertheless the optimization program was employed to see if a systematic trend was observable. The values for symmetrical elements turned out to be the same in the whole temperature range. The values of the double layer capacitance remained relatively low. The values of the pseudocapacitances C2 and C7 became too large above 250°C, when compared with the values of the double layer capacitances. Finally the resistance R5 was found larger than the computed bulk resistance. The results of the computations confirm the statement in the beginning of this

paragraph.

The change in the shape of the frequency spectrum of the cell impedance, observed between 150 and 200°C on cells with saw-cut surfaces of the solid electrolyte, is different from the change for cells with polished surfaces. Essentially, the phase angle becomes nearly independent of frequency and assumes relatively small values. The effect of the bulk resistance of the solid electrolyte on the absolute value of Z_{cell} is clearly recognizable up to 300°C. Then the absolute value of the impedance does not vary much with frequency any more. An analysis of the experimental data by the network in Fig.4 becomes difficult with increasing temperature because of the small values of the phase angle at larger temperatures. It is interesting to note that the optimization program begins to yield the same values for symmetrical components of the network, starting at 200°C. The resistance R5 makes a relatively large contribution to the total impedance at 200 and 250°C. Therefore the network analysis gives the bulk resistance of the solid electrolyte in a first approximation. Above 300°C the ohmic component of the cell impedance at 10^4 Hz is very close to the value of the bulk resistance, computed from the dimensions and the four-probe conductivity. The cells with saw-cut surfaces display the behavior of a cell with non-blocking electrodes.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS.

- Fig.1: Setup of the cell Ag/Ag beta"alumina/Ag.
- Fig.2: Impedance spectra of the cell with polished surfaces of the solid electrolyte at different temperatures.
- Fig.3: Impedance spectra of the cell with saw-cut surfaces of the solid electrolyte at different temperatures.
- Fig.4: Analogue network for the cell.
- Fig.5: Results of the approximation of the experimental data in Fig.2, 50°C by the network in Fig.4 (solid curves).

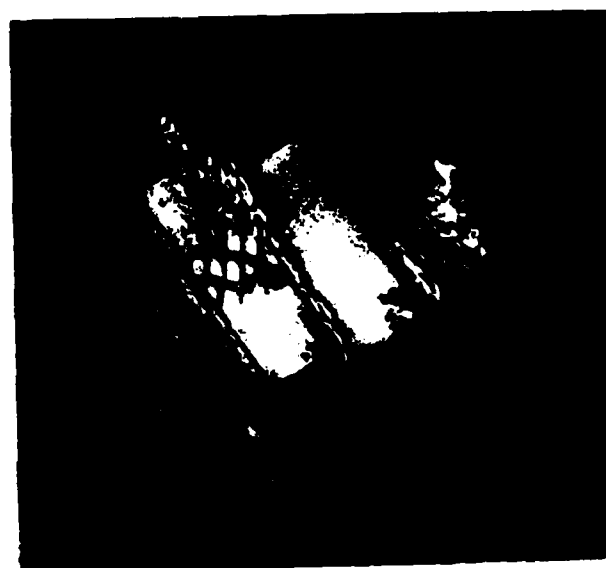
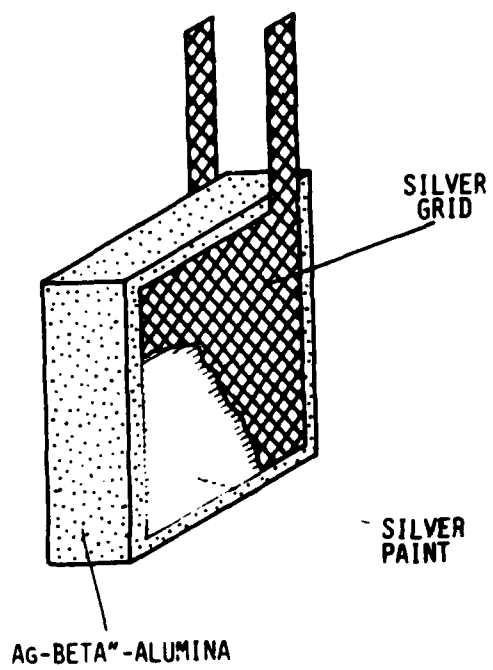


Fig.1

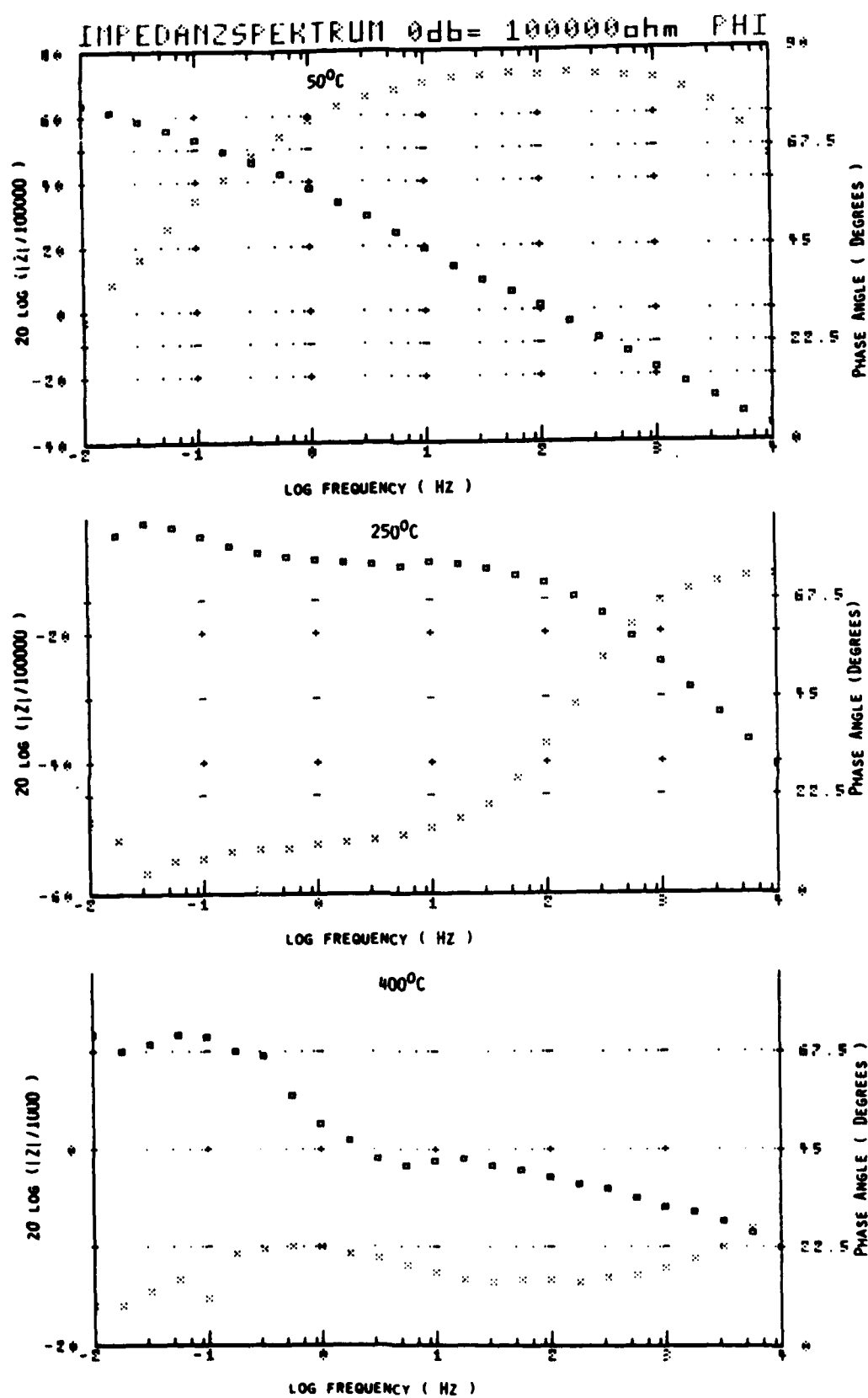


Fig.2

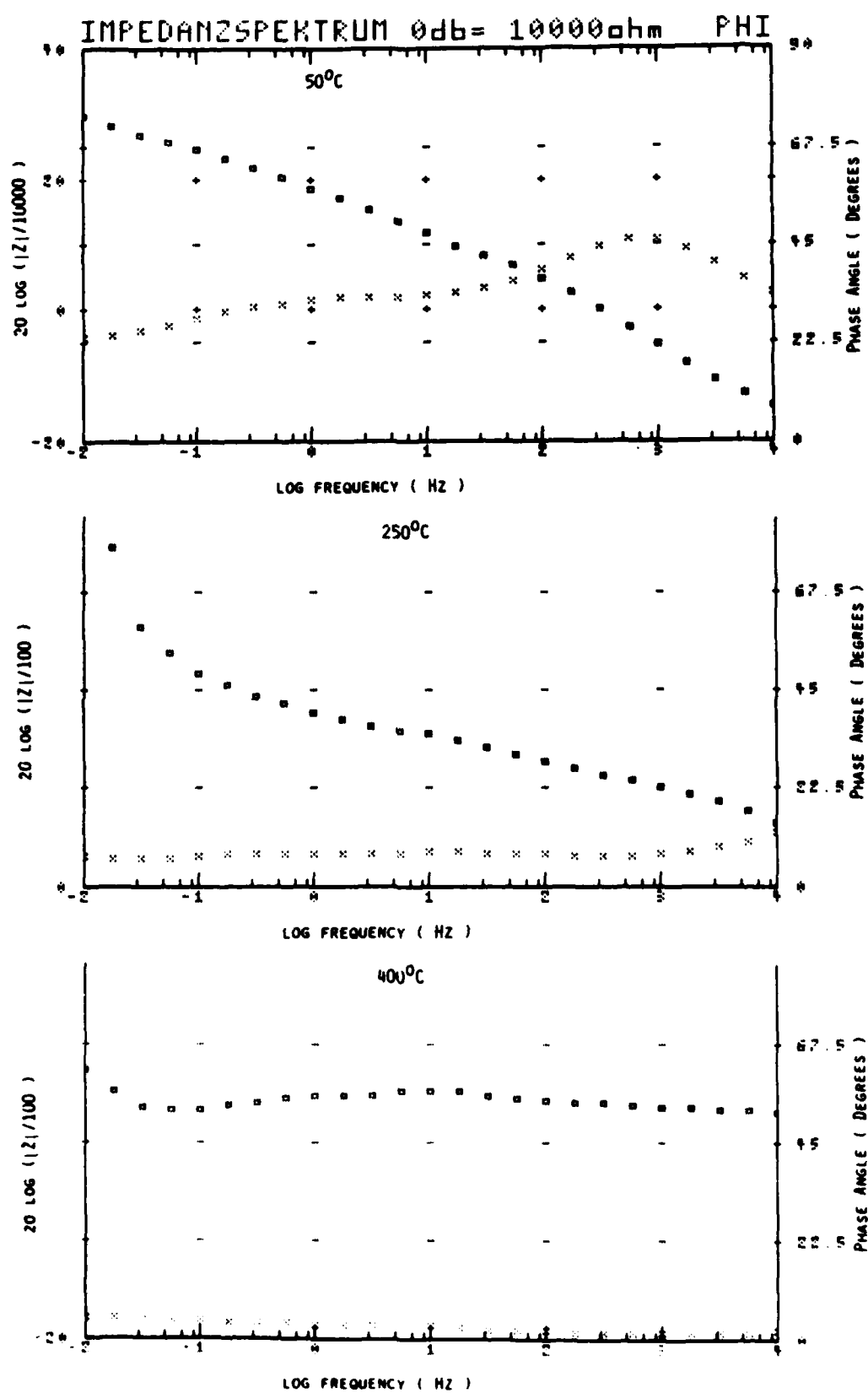


Fig. 3

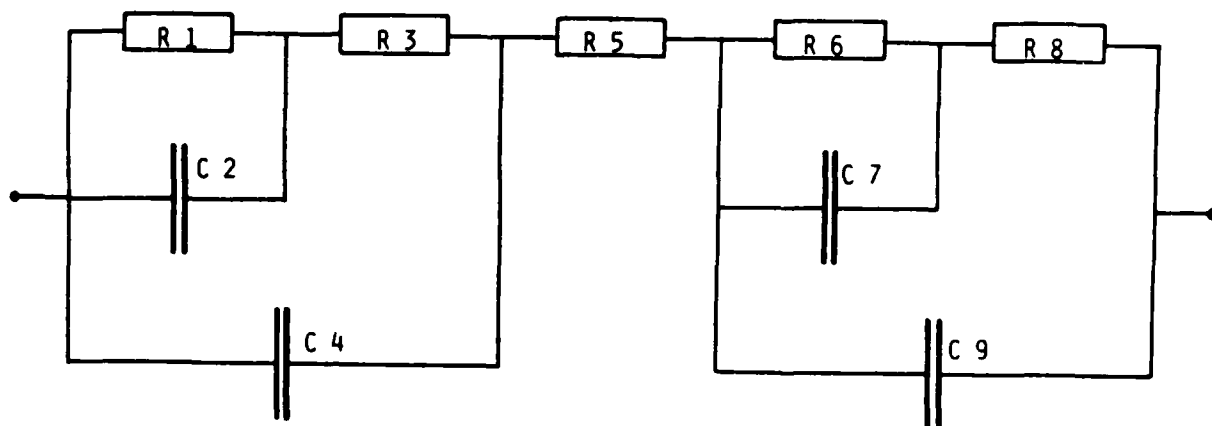


Fig.4

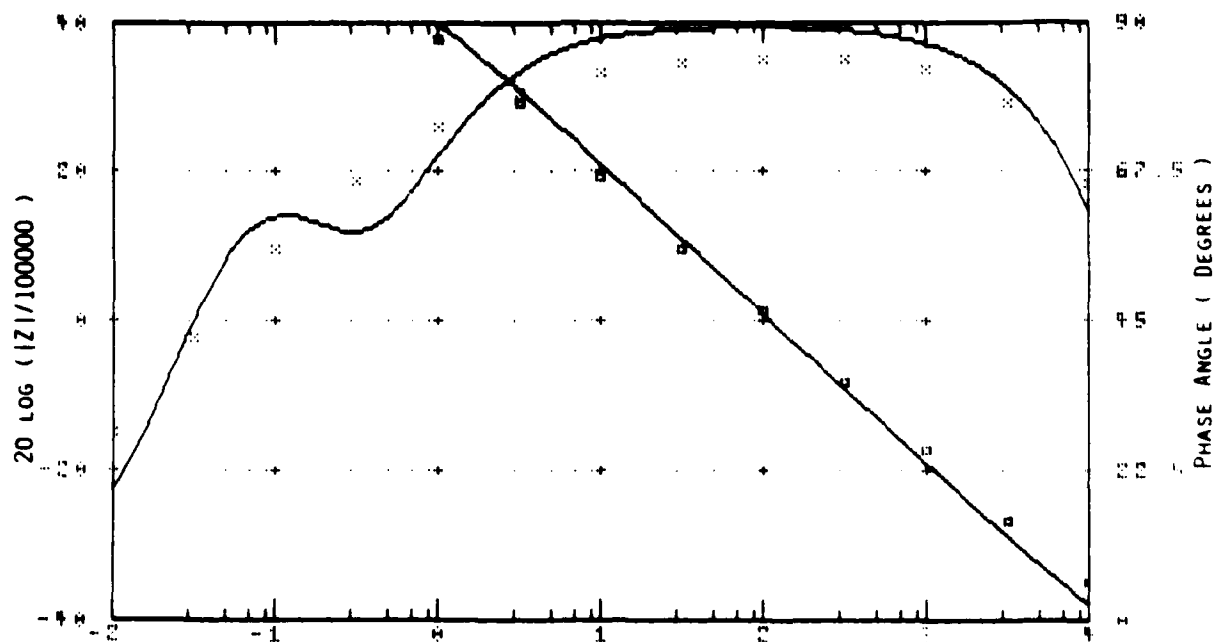


Fig.5

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